Defects and Impurities in Semiconductor Growth

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High Doped p-Type GaN Grown by Alternative Co-Doping Technique

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ABSTRACT

We investigated the electrical properties of Mg-doped GaN grown by alternative pulse supplies of source and dopant materials in metalorganic vapor phase epitaxy. We obtained the hole concentration of $6x10^{18}cm^{-3}$ for p-type GaN grown on a sapphire substrate by repetition of supply and purging of Ga and Mg sources in the constant NH_3 flow, while that of p-type GaN grown by the constant feeding of Ga and Mg sources was $2x10^{18}cm^{-3}$. By using alternative feedings of Ga source and NH_3 with Mg-Si co-doping, we obtained a highly hole concentration of $2x10^{19}cm^{-3}$ for p-type GaN which was grown directly on a low temperature AlN buffer layer. We also obtained the hole concentration of $6x10^{18}cm^{-3}$ for p-type GaN which was grown on an AlGaN layer on a SiC substrate by alternative co-doping technique. The activation energies for Mg-doped GaN grown by the pulse feedings of source materials were lower than that for GaN grown by continuous supplies of source materials as used in the conventional technique.

INTRODUCTION

Realization of highly conductive p-type GaN and AlGaN is essentially important for optical and electrical devices using nitride compounds. High conductive p-type cladding and contact layers are necessary for ultraviolet light emitting diodes (LEDs) and laser diodes (LDs). For wide-bandgap semiconductors, it is difficult to realize high conductivity p-type layer because of the large activation energy of acceptor impurities. Co-doping is theoretically proposed to get high hole concentration in p-type GaN and AlGaN [1]. According to the previously reported theory, donor and acceptor impurities are doped simultaneously and acceptor-donor-acceptor complexes are formed. In this case, compensation should be avoided and the activation energy of acceptor should be reduced by the formation of complexes. Co-doping in GaN has been reported.[2-6]. However, it is difficult to get highly doped p-type GaN by conventional co-doping technique. If p-type and n-type impurities are supplied at the same time in continuous feeding of source materials, donor and acceptor atoms will be distributed randomly in the crystal and compensation is supposed to occur.

In this paper, application of atomic layer epitaxy (ALE) is proposed for doping two impurity atoms in the desired configuration. In ALE growth of GaN, source materials are fed alternatively into a reactor [7,8]. In our study, p-type GaN layers are grown by two different techniques in which pulse supplies of source and dopant materials are performed in a low pressure metalorganic vapor phase epitaxy (MOVPE). Hole concentrations of p-type GaN layers are compared with Mg-doped GaN grown by continuous supplies of source materials as used in conventional growth technique. The activation energies are also compared with that of Mg in GaN grown by conventional technique.

EXPERIMENTAL DETAILS

GaN epitaxial layers were grown on c-face (0001) sapphire substrates and SiC substrates in a horizontal reactor at a pressure of 76 Torr. The source materials were TMGa (trimethylgallium), TMAl (trimethyl aluminum) and NH_3 (ammonia). The p-type dopant source was Cp_2Mg (bis-cyclopentadienyl magnesium) and the n-type dopant source was TESi (tetraethyl silane). The main flow gas through the reactor was 5 slm of H_2 mixed with 2 slm of N_2. Prior to the epitaxial growth, the substrate was thermally cleaned in situ at 1200°C. Typical sequential supplies of source and dopant materials are shown in figure 1(a) and 1(b).

Figure 1(a) shows the growth mode in which GaN was grown by repetition of 2 sec feeding and 2 sec interval of TMGa in constant NH_3 flow. Mg dopant source was supplied during the TMG feeding periods. P-type GaN layer was grown on an undoped AlGaN layer which was grown at 1130°C on a low temperature (LT)-AlN buffer layer. The LT-AlN buffer layer was deposited at 600°C for 3 min on a sapphire substrate.

Figure 1(b) shows the growth mode in which GaN was grown by alternating supply of TMG and NH_3 with a sequence of 1 sec feed and 3 sec interval for each source gas. A main 1 slm NH_3 was alternatively supplied with H_2 to minimize the pressure fluctuation inside the reactor. A small amount of NH_3 flow of 50 sccm was continuously fed into a reactor to suppress the desorption of nitrogen from the GaN surface during the stop of the main NH_3 flow. Mg source gas was simultaneously fed with TMGa and Si source gas was fed just after the feeding of Mg source.

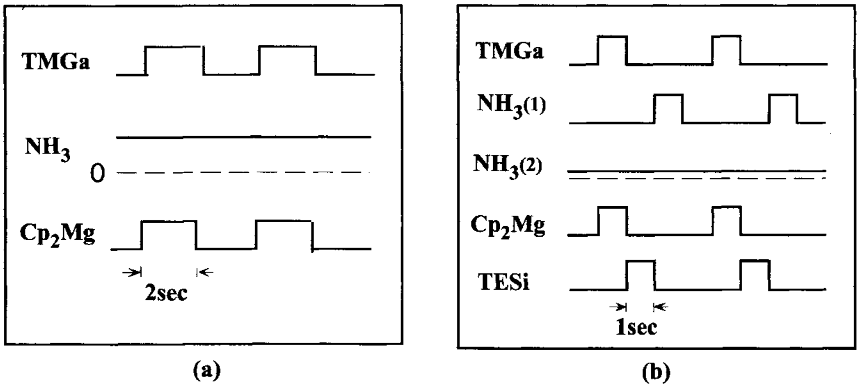

Figure 1. Sequential pulse supplies of source and dopant materials. **(a)** Pulse supplies of TMGa and Cp_2Mg in continuous NH_3 flow. **(b)** Alternative supply of TMGa and NH_3 (1) in a small amount of continuous NH_3 (2) flow. Cp_2Mg was supplied during the TMGa feeding time and TESi was supplied just after the Cp_2Mg feeding time.

The Mg-doped GaN samples were annealed at 750°C in N_2 ambience for 25 min after the epitaxial growth. Ni/Au electrodes were evaporated on the sample surface to form the ohmic contacts for Hall measurement. The hole concentrations of the epitaxial layers were measured by van der Pauw method at temperatures from 300K to 500K. The activation energy of the Mg acceptor was estimated from the temperature dependence of hole concentration. Photoluminescence (PL) spectra at 77K were measured to evaluate the crystal quality of epitaxial layers.

RESULTS AND DISCUSSION

GaN grown by pulse feeding of TMGa and Cp_2Mg in constant NH_3 flow

P-type GaN layers were grown at 1050°C on an AlGaN buffer layer of 0.4 µm thickness by pulse feedings of TMGa and Cp_2Mg in constant NH_3 flow of 1 slm, as shown in figure.1(a). Figure 2 shows the hole concentration at 300K as a function of Cp_2Mg flow rate at growth temperature of 1050°C for the TMGa flow rate of 2.5 sccm. Open circles in figure 2 show the hole concentration in GaN grown by pulse feeding method. The hole concentration increases with the increase of Cp_2Mg flow rate and has a maximum value of $6x10^{18}cm^{-3}$ at the flow rate of $5x10^{-8}$mol/min. Closed circles, (2), shows the hole concentrations of GaN grown by continuous feeding of TMG at 1050°C. The hole concentration increased and saturated at $2x10^{18}cm^{-3}$ with increasing of Cp_2Mg supply. This result indicates that high hole concentration was obtained by the pulse feeding of Cp_2Mg.

Figure 3 shows the temperature dependence of the hole concentrations of Mg-doped GaN in the temperature range from 300K to 500K. Open circles and squares in figure 3 show the hole concentrations of GaN grown by pulse feeding method for two different Cp_2Mg flow rate. For two samples, the temperature dependence yielded 160meV for the activation energy of Mg. Closed circles, (3), show the

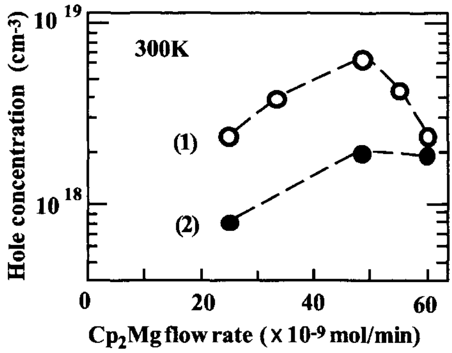

Figure 2. Hole concentrations at 300K as a function of the Cp_2Mg flow rate. (1) shows the hole concentrations of p-GaN grown by pulse supplies of TMGa and Cp_2Mg in constant NH_3 flow. (2) shows the hole concentrations of p-GaN grown by continuous supplies of TMGa and Cp_2Mg.

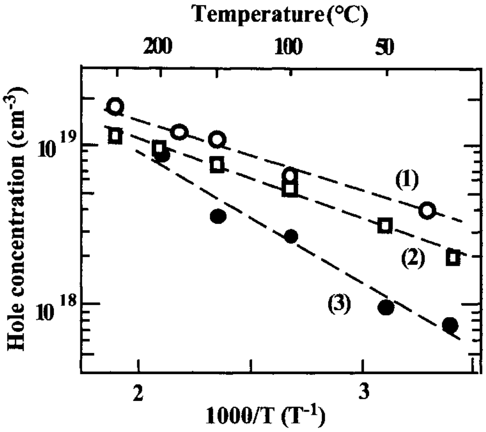

Figure 3. Temperature dependencies of hole concentration of Mg-doped GaN grown by pulse supplies of TMGa with (1) $3.4x10^{-8}$ and (2) $2.5x10^{-8}$mol/min of Cp_2Mg in constant NH_3 flow. (3) shows the hole concentrations of GaN grown by continuous feedings of TMGa, NH_3 and $2.5x10^{-8}$mol/min of Cp_2Mg.

hole concentrations of GaN grown by the continuous feedings of TMGa and Cp_2Mg. The activation energy for the continuous feeding GaN was 240meV. These results indicate that the activation energy was reduced in GaN grown by pulse feeding of Cp_2Mg. Depth profile of Mg density in the GaN layer grown by pulse feeding was measured by SIMS (secondary ion mass spectroscopy). Mg density decreased abruptly with the depth from the surface. Internal electrical field caused by the large gradient of Mg density seems to reduce the activation energy of Mg.

<u>GaN grown by alternative co-doping on a sapphire substrate</u>

Co-doped GaN was grown by TMGa, NH_3,Cp_2Mg and TESi at 950°C, as shown in figure 1(b). In this case, the GaN epitaxial layer of 0.3 µm thickness was grown directly on an LT-AlN buffer layer on a sapphire substrate. A small amount of NH_3 was continuously fed into reactor to suppress the desorption of nitrogen from GaN surface. By using similar growth sequence, undoped GaN was grown directly on the LT-AlN buffer layer at 950°C. In PL spectra from the undoped GaN, the intensity of band edge emission was strong in comparison with the yellow band emission due to deep levels. This result indicates that high quality layer of GaN grown directly on a LT-AlN buffer layer can be obtained by the alternative feeding method without an AlGaN buffer layer.

Cp_2Mg was supplied during the feeding time of TMGa while TESi was supplied in the purging time of TMGa before NH_3 feeding time, as shown in figure 1(b). Carrier type and concentration of GaN strongly depended on the TMGa flow rate, as shown in figure 4. Highly conductive p-type GaN was obtained at the TMGa flow rate of 8µmol/min. Hole concentration and mobility of p-type GaN were $2x10^{19}cm^{-3}$ and 0.2 $cm^2V^{-1}s^{-1}$, respectively. Below this flow rate of TMGa, highly resistive GaN was

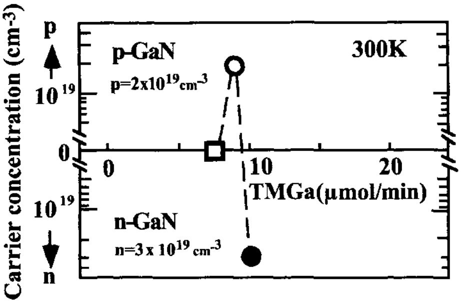

Figure 4. Carrier concentrations at 300K for GaN layers grown by alternative supplies of TMGa and NH_3 against the TMGa flow rate. An open circle shows the p-type GaN, a closed circle shows the n-type GaN and a square shows the highly resistive GaN.

obtained. Above 10 μmol/min of TMGa flow rate, highly conductive n-type GaN was obtained even if a large flow of Cp_2Mg was supplied. For n-type GaN, carrier concentration and mobility were $3x10^{19}cm^{-3}$ and 6 $cm^2V^{-1}s^{-1}$, respectively. Thus, highly conductive p-type GaN was obtained within a narrow range of TMGa flow rate.

Figure 5 shows the hole concentrations of p-type GaN in the temperature range from 300K to 500K. The temperature dependence for the Mg-Si doped GaN, shown by (1), yielded 60meV for the activation energy of acceptor. On the other hand, the activation energy obtained from the temperature dependence of

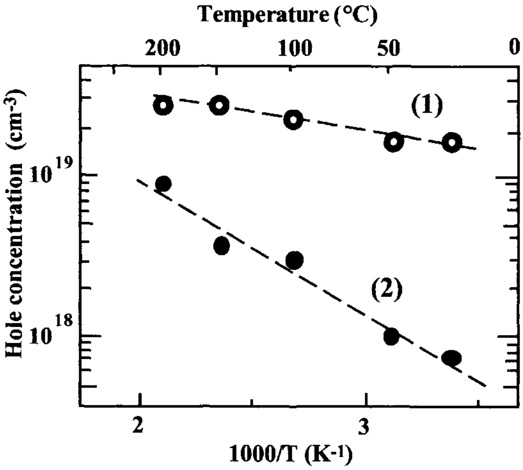

Figure 5. Hole concentration as a function of temperature. (1) shows the hole concentration of p-GaN grown by alternative co-doping of Mg and Si. (2) shows the hole concentration of p-GaN grown by continuous supplies of TMGa , NH_3 and Cp_2Mg.

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hole concentration in p-type GaN grown by conventional method was 240meV, as shown by (2). Thus, the activation energy of acceptor in GaN grown by the alternative co-doping method is much smaller than that of Mg in GaN grown by conventional growth technique. However, it was difficult to obtain highly conductive p-type GaN grown by the alternative co-doping technique on a AlGaN buffer layer on a sapphire substrate under the same condition at present.

GaN grown by alternative co-doping on a SiC substrate

GaN was grown on a SiC substrate by using an alternative feeding of TMGa and NH_3 at 950°C, as shown in figure 1(b). GaN layers were grown on an undoped AlGaN layer of 0.2 μm thickness. PL spectra were measured to examine the crystal quality of undoped GaN grown by alternative feeding of TMGa and NH_3. High quality GaN was obtained at the TMGa feeding rate of 2.5 sccm and the main NH_3 flow rate of 1 slm. The continuous NH_3 flow of 50sccm was necessary to keep the crystal quality.

Cp_2Mg was supplied during the feeding time of TMGa while TESi was supplied during purging time of TMGa before NH_3 feeding time, as shown in figure 1(b). Figure 6 shows the hole concentrations of co-doped GaN as a function of the TESi flow rate. The Mg supply was kept constant at $1.2x10^{-8}$mol/min. The hole concentration of Mg-doped GaN without Si dopant was $2.4x10^{18}cm^{-3}$. With the increase of TESi flow rate in the constant Mg feeding rate, the hole concentration decreased slightly due to the compensation for a TESi flow of $5x10^{-9}$mol/min. With the further increase of TESi to the flow rate of $8x10^{-9}$mol/min, hole concentration increased to $6x10^{18}cm^{-3}$ with the mobility of 0.5 $cm^2V^{-1}sec^{-1}$. By introducing the optimum amount of Si together with Mg dopant , the hole concentration was increased more than that of p-type GaN without Si dopant. The Mg and Si densities in the GaN layer were $2x10^{19}$ cm^{-3}, as measured by SIMS.

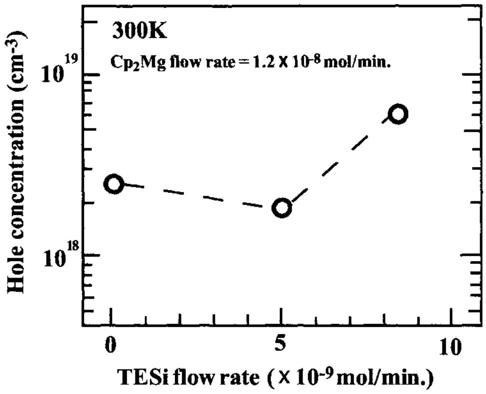

Figure 6. Hole concentration of Mg-doped GaN grown on a SiC substrate as a function of TESi flow rate. TESi was fed just after the feeding of Cp_2Mg in the purging time of TMGa before NH_3 feeding time. The flow rate of Cp_2Mg was $1.2x10^{-8}$mol/min.

In the TMGa feeding period, Si and Mg can migrate on the Ga surface and can make a complex that will act as a shallow acceptor, as predicted by the reported theory. When Mg and Si are used as dopants with TMGa and NH_3, they cannot migrate so easily and the complex is difficult to make. The migration of Mg and Si on the Ga-rich surface in the ambience of the small amount of NH_3 is essential to achieve the co-doping effect.

CONCLUSIONS

Mg-doped GaN layers grown on sapphire substrates by pulse feedings of Ga and Mg sources in MOVPE showed high hole concentrations at room temperature. The hole concentration of $6x10^{18}cm^{-3}$ was obtained for GaN grown on an AlGaN buffer layer by pulse supplies of TMGa and Cp_2Mg in constant NH_3 flow. By alternative feedings of TMGa and NH_3 with the alternative co-doping of Mg and Si , p-type GaN grown on an LT-AlN showed the hole concentration of $2x10^{19}cm^{-3}$. P-type GaN layers doped with Mg and Si on SiC substrates also showed the hole concentration of $6x10^{18}$ cm^{-3}. The activation energies for Mg-doped GaN grown by pulse feedings of source materials were lower than that for GaN grown by the conventional growth method.

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